CHEMICAL CHANGES PRODUCED IN COAL THROUGH
THE ACTION OF LEWIS ACID CATALYSTS

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INTRODUCTION

Molten Lewis acids and in particular $ZnCl_2$ and $SnCl_2$ are known to catalyze the conversion of coal to liquid products [1-15]. While the degree of liquefaction attainable with different catalysts is known, the manner in which Lewis acids promote liquefaction is not well understood. The present work was undertaken in an effort to establish more clearly the effects of Lewis acids on coal and to identify the specific chemical reactions which these catalysts affect. The results reported here concern experiments conducted with both solvent refined coal (SRC) and a variety of model compounds. The latter were selected to represent the aliphatic, ether, and sulfide linkages which connect the aromatic and hydro-aromatic groups in coal. Several models of fused ring aromatic clusters were also examined.

EXPERIMENTAL

Apparatus

All reactions were conducted in a 300 cm^3 stirred autoclave (Autoclave Engineers, Inc. Model ABP-300). To facilitate the introduction of reactants and the removal of products a snugly fitted glass liner was used to contain the reaction mixture. The temperature and pressure within the autoclave were recorded continuously.

Materials

The SRC used here was produced from a bituminous West Kentucky coal by the Pittsburg and Midway Coal Mining Company in Tacoma, Washington. The SRC was dried overnight in an N_2-purged oven at 105°C and then ground to pass through an 80 Tyler mesh sieve. The sieved SRC was then stored in a vacuum dessicator until needed for a run.

Model compounds were obtained from a variety of standard commercial sources. These materials were kept dry but were not purified before use.

Lewis acid catalysts were also obtained from several sources. Since several of these materials are hygroscopic (viz. $AlCl_3$, $FeCl_3$, $SbCl_3$) the catalysts were first dried in a vacuum oven overnight at 105°C and then stored in an N_2-purged dry box. Weighing of the catalyst and transfer into the glass liner were also carried in the dry box.

Product Analysis

The liquid products obtained from reactions of SRC were disengaged from the reaction solvent and dried. The dried material was then weighed to establish the fraction of the SRC submitted to reaction which had been converted to liquid products. The stoichiometry of the dissolved products was determined by elemental analysis and the ratio of aliphatic to aromatic hydrogens, H_{Al}/H_{Ar}, by ^{1}H-NMR.

The products obtained from model compound studies were analyzed by gas chromatography. Product identification was established with the aid of a gas chromatograph/mass spectrometer. Where possible product assignments were confirmed by injecting pure compounds into the gas chromatograph/mass spectrometer and comparing their retention times and mass spectra with those of the postulated reaction product.

RESULTS AND DISCUSSION

SRC Studies

Table 1 summarizes the results of screening experiments designed to compare the influence of selected Lewis acid catalysts on the dissolution of SRC in benzene at 300°C. It is apparent that the stronger acids, $AlCl_3$, $FeCl_3$, $SbCl_3$, and $HgCl_2$, cause a decrease in SRC solubility over that obtained without a catalyst. The use of $ZnCl_2$ does not alter the benzene solubility of SRC but contributes significantly to raising the H/C and H_{Al}/H_{Ar} ratios of the soluble product. Similar results were obtained with $SnCl_2$ but in this instance a greater fraction of the SRC was dissolved. These results suggest that the acidity of the catalyst should be high enough to promote bond cleavage but not so high as to catalyze rapid retrograde reactions which lead to a diminished solubility of SRC.

The effectiveness of a given catalyst on the solubilization of SRC also depends upon the solvent as shown in Table 2. Here, it is seen that while cyclohexane is a less effective solvent for SRC than benzene, the introduction of either $ZnCl_2$ or $SnCl_2$ into cyclohexane has a very pronounced effect on the yield of soluble products.

Model Compound Studies

The cleavage of aliphatic linkages between aromatic nuclei was studied using the model compounds listed in Table 3. To facilitate product identification, cyclohexane was used as the solvent. Reactions were typically carried out for 90 min. at 325°C and 1000 psig of H_2. The ratio of substrate to catalyst was usually 14.3 mole/mole.

Screening studies performed on the unsubstituted diphenyl alkanes showed that the cleavage of the aliphatic bridge in these compounds required the use of a strong Lewis acid such as $AlCl_3$. In the presence of this catalyst diphenyl methane, ethane, propane, and butane reacted readily at temperatures as low as 250°C. The initial products were always bezene and a phenyl alkane, indicating that cleavage had occurred between a benzene ring and the first carbon of the aliphatic bridge. The phenyl alkane product was not stable, however, and was observed to isomerize or crack to shorter chained products. In the cases of diphenyl propane and diphenyl butane, indan and tetralin were observed respectively as major reaction products. While 70 to 80% of the diphenyl alkanes were converted to products under the conditions noted earlier, diphenyl was less reactive and was only 32% converted. The only product obtained from diphenyl was benzene.

A mechanism which summarizes our observations on the cleavage of diphenyl and the diphenyl alkanes is shown below. The lower reactivity of diphenyl is explained by the fact that the phenyl carbonium ion, formed in the first step of the reaction, is less stable than a phenyl alkane carbonium ion.

The addition of a hydroxyl group to one of the phenyl rings of diphenyl methane was found to contribute an inductive effect, facilitating cleavage of the aliphatic linkage. Since phenol was a major reaction product it was concluded that cleavage had occurred preferentially at the ring containing the hydroxyl group. Experiments were also performed to determine whether the inductive effect of the hydroxyl group would now permit $ZnCl_2$, a weaker Lewis acid, to cleave the aliphatic bridge. These experiments gave positive results. However, under identical reaction conditions $ZnCl_2$ provided only half of the substrate conversion obtained with $AlCl_3$.

To determine the effects of fused ring nuclei upon the cleavage of aliphatic bridges, experiments were conducted with phenyl naphthalene and benzyl naphthalene. By analogy with diphenyl, phenyl naphthalene was relatively unreactive and could be cleaved only to the extent of 10%. Benzyl naphthalene, on the other hand, was completely converted to naphthalene, benzene, and other aromatic products. The reaction of benzyl naphthalene in the presence of $ZnCl_2$ was also examined. It was found that while $ZnCl_2$ is not as effective a catalyst as $AlCl_3$ it would bring about a 40% conversion of the substrate to products.

The cleavage of ether and sulfide linkages occurred more readily than the cleavage of aliphatic linkages and could be catalyzed by $ZnCl_2$. Reaction of diphenyl ether at 325°C yielded phenol and benzene. Under similar conditions diphenyl sulfide yielded thiophenol and benzene. Dibenzyl ether and dibenzyl sulfide followed similar reaction paths. Both of these substrates apparently form benzyl carbonium ions which rapidly alkylate the solvent, benzene, to produce diphenyl methane.

The reactions of benzyl naphthyl ether were also explored. In benzene this substrate yielded 2-hydroxynaphthalene and diphenyl methane. These products again illustrate the preferential cleavage of the linkage to produce a benzyl carbonium ion.

The effects of Lewis acid catalysts on fused ring aromatic clusters was also examined, using naphthalene and phenanthrene as models. In the presence of $AlCl_3$, naphthalene was converted to tetralin which in turn cracked to produce benzene. Phenanthrene reacted to produce 9,10-dihydrophenanthrene and smaller quantities of naphthene and tetralin. Thus both naphthalene and phenanthrene appear to react by first hydrogenating and then cracking to produce products of lower molecular weight. It is interesting to note that for temperatures up to 325°C no evidence was obtained that $ZnCl_2$ could promote reactions similar to those observed with $AlCl_3$.

CONCLUSIONS

The following conclusions can be drawn from this work.

- $ZnCl_2$ and $SnCl_2$ are particularly suitable catalysts for the dissolution of SRC in benzene and cyclohexane.

- The strength of acid required to catalyze the cleaveage of aliphatic linkages between aromatic nuclei depends upon the nature of the nuclei, naphthyl and hydroxyphenyl groups being more readily separated from aliphatic linkages than phenyl groups.

- Ether and sulfide linkages are easily cleaved by mild Lewis acids such as $ZnCl_2$.

- The products obtained from the cleavage of aliphatic, ether, and sulfide linkages can be explained by carbonium ion mechanisms.

- Hydrogenation and cracking of fused ring aromatic clusters requires strong Lewis acids such as $AlCl_3$.

ACKNOWLEDGMENT

REFERENCES

(1) C. O. Hawk and R. W. Hiteshue, U.S. Bureau of Mines
     Bulletin No. 622(3), 1965.

(2) C. W. Zielke, R. T. Struck, J. M. Evans, C.P.. Costanza,
     and E. Gorin, Ind. Eng. Chem. Process Des. Dev., 5(2),
     151 (1966).

(3) C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza,
     and E. Gorin, Ind. Eng. Chem. Process Des. Dev., 5(2),
     158 (1966).

(4) W. Kawa, S. Friedman, L. V. Frank; and R. W. Hiteshue,
     Preprints, ACS Fuel Chem., Am. Chem. Soc., 12(3) 4347 (1968).

(5) Research on Zinc Chloride Catalyst for Converting Coal to
     Gasoline, Research and Development Report No. 39, Vol. III,
     Books 1,2, prepared by the Consolidation Coal Company for
     the Office of Coal Research, 1968.

(6) R. T. Struck, W. F. Clark, P. J. Dudt, W. A. Rosenhoover,
     C. W. Zielke, and E. Gorin, Ind. Eng. Chem. Process Des.
     Dev., 8(4), 546 (1969).

(7) C. W. Zielke, R. T. Struck, and E. Gorin, Ind. Eng. Chem.
     Process Des. Dev., 8(4), 552 (1969).

(8) W. Kawa, H. F. Feldmann, and R. W. Hiteshue, Preprints,
     ACS Fuel Chem., Am. Chem. Soc., 14(4), Part 1, 19 (1970).

(9) Project Western Coal: Conversion of Coal Into Liquids –
     Final Report, Research and Development Report No. 18,
     prepared by the University of Utah for the Office of
     Coal Research, May 1970.

(10) S. A. Qader, K. Duraiswamy, R. E. Wood, and G. R. Hill,
     AIChE Symposium Series, 69(127), 102 (1973).

(11) Coal Processing – Gasification, Liquefaction,
     Desulfurization: A Bibliography 1930–1974, Atomic
     Energy Commission, October 1974.

(12) H. Katzman, A Research and Development Program for
     Catalysis in Coal Conversion Processes, Electric Power
     Research Institute Report No. 207-0-0, Palo Alto, Calif.,
     1974.

(13) C. W. Zielke, W. A. Rosenhoover, and E. Gorin,
     Preprints, Div. of Fuel Chem., Am. Chem. Soc., 19(2)
     306 (1974).

(14) D. S. Ross and J. Y. Low, "Homogeneous Catalysis – Acid
     Catalysis", in Homogeneous Catalytic Hydrocracking
     Processes for Conversion of Coal to Liquid Fuels, Stanford
     Research Institute, Menlo Park, Calif., Quarterly Report
     Nos. 2,3, 1976.

(15) R. E. Wood and W. H. Wiser, <u>Ind. Eng. Chem. Process</u>
      <u>Des. Dev.</u>, <u>15</u>(1), 144 (1976).

Table 1

Effects of Lewis Acid Catalysts on
the Liquefaction of SRC in Benzene

Reaction Conditions: T = 300°C   Catalyst mass = 5 gm
                       P = 2000 psig H_2 SRC mass = 5 gm
                       t = 90 min   Solvent volume = 70 ml
                       ω = 1250 rpm

Catalyst	Sol. (%)	Charac. of Sol. Prod. H/C	H_{Al}/H_{Ar}
None	46.7	0.85	1.33
$AlCl_3$ [a]	20.3	0.89	1.32
$ZnCl_2$	46.8	1.01	2.54
$SnCl_2$	57.9	0.97	2.22
$SbCl_3$	38.2	0.95	2.18
$HgCl_2$	37.8	0.93	1.79

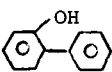[a] 1.0 gm $AlCl_3$ charged

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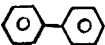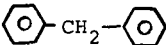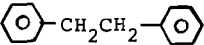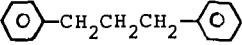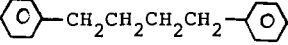
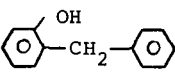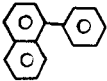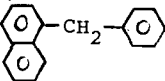Table 2

Effects of Solvents on the Liquefaction of SRC

Reaction Conditions: T = 300°C   Catalyst mass = 5 gm
                       P = 2000 psig H_2 SRC mass = 5 gm
                       t = 90 min   Solvent volume = 70 ml
                       ω = 1250 rpm

Catalyst	Solvent	Sol. (%)	Charac. of Sol. Prod. H/C	H_{Al}/H_{Ar}
None	Benzene	46.7	0.85	1.33
None	Cyclohexane	15.1	0.91	1.50
$ZnCl_2$	Benzene	46.8	1.01	2.54
$ZnCl_2$	Cyclohexane	35.4	1.06	3.38
$SnCl_2$	Benzene	57.9	0.97	2.22
$SnCl_2$	Cyclohexane	29.8	1.00	2.68

Table 3

Model Compounds Containing Aliphatic Linkages

Compound	Structural Formula
Diphenyl	⬡—⬡
Diphenyl methane	⬡—CH$_2$—⬡
1,2-Diphenyl ethane	⬡—CH$_2$CH$_2$—⬡
1,3-Diphenyl propane	⬡—CH$_2$CH$_2$CH$_2$—⬡
1,4-Diphenyl butane	⬡—CH$_2$CH$_2$CH$_2$CH$_2$—⬡
2-Phenyl phenol	⬡—⬡—OH
2-Benzyl phenol	⬡—CH$_2$—⬡ (OH)
1-Phenyl naphthalene	⬡⬡—⬡
1-Benzyl naphthalene	⬡⬡—CH$_2$—⬡